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(54) Title: PHOSPHORS WITH IMPROVED LUMEN OUTPUT AND LAMPS MADE THEREFROM

(57) Abstract

A phosphor having a continuous protective bi-layer coating of alumina surrounding silica surrounding the phosphor particles is disclosed. The method of making a bi-layer coating on phosphor particles is also disclosed. The first layer surrounding the phosphor is silica. The second layer surrounding the phosphor is alumina. The bi-layer phosphor is useful in fluorescent lamps providing improved maintenance and brightness. The bi-layer phosphor can also be used in high color rendition lamps employing blends of phosphors.

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PHOSPHORS WITH IMPROVED LUMEN OUTPUT
AND LAMPS MADE THEREFROM

The present invention relates to improved manganese
5   activated zinc silicate phosphors. More specifically, the
present invention involves coating a willemite phosphor
with a layer of silica and then a coating of alumina. The
"bi-layer" phosphor obtained shows improved lumen
characteristics and is particularly useful in fluorescent
10 lamps.

During certain phosphor synthesis and lamp fabrication
steps, the finely divided luminescent materials may be
exposed to oxidizing (oxygen-rich) atmospheres at elevated
15 temperatures. An example of this is the so-called
'lehring' process used to burn away organic aqueous lamp
coating dispersion. It is well known that the brightness
of the finished fluorescent lamp may be reduced
significantly as a result of the lehring operation (the
20 so-called 'lehrloss'). This reduction in brightness may
result from a partial oxidation of reactive low valence
ions present in the phosphor lattice.

A somewhat more involved example relates to the
process in U.S. Patent 4,585,673 wherein the formation of
25 protective coatings (typically alumina coatings) upon the
surfaces of finely divided phosphor particles via chemical
vapor deposition using an organometallic precursor in a
gas-fluidized bed is disclosed. When manganese-doped zinc
silicate is alumina-coated via the process described in
30 the '673 patent, and when fluorescent lamps are fabricated
from the coated phosphor produced therefrom, these lamps
display much better lumen maintenance than do similar
lamps fabricated using the virgin (uncoated) zinc silicate
phosphor. During the fabrication of such lamps, the
35 phosphor particles are typically dispersed in an aqueous
medium. Unfortunately, if the water-based suspension is

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held-over for several days before use (a typical
situation), the beneficial effects associated with the
'673 coating are lost.

　　　This 'holdover' problem can be overcome, however, by
5　annealing the alumina-coated phosphor in the air at a
temperature between about 700°C and about 850°C for a
period of time ranging from about 15 minutes to about 20
hours as described in U.S. Patent 4,805,400.
Unfortunately, while this coated phosphor annealing
10　process solves the holdover problem, it also causes the
zinc silicate phosphor to react with the alumina coating.
Zinc and manganese diffuse into the alumina coating,
probably forming a mixture of zinc and manganese
aluminates. The coated phosphor develops a 'body color',
15　and suffers a reduction in visible light emission upon
exposure to an ultraviolet light source. Moreover, very
similar phenomena are observed, as well, when the virgin
(uncoated) phosphor is subjected to the annealing process.
The increased body color and reduced brightness which
20　result from annealing both the uncoated and the '673
coated zinc silicate phosphor are believed to partially
result from the oxidation of some of the divalent
manganese ions located on the surface of the uncoated
phosphor particles or within and on the surface of the
25　reactive alumina coating.

　　　Prior to the present invention, there was no known
means of preventing these detrimental interactions between
the phosphor and the oxygen-rich atmosphere within the
annealing furnace. By means of the method described
30　below, these detrimental interactions are virtually
eliminated, allowing a phosphor coated by the process
disclosed in the '673 patent to be thoroughly annealed
without suffering reflectance or brightness losses.

　　　Another aspect of the present invention involves the
35　use of high brightness zinc silicate phosphors as
components of the triblend phosphors. As discussed

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previously, coated zinc silicate phosphors are unstable in
the water based suspension systems used to manufacture
fluorescent lamps. The zinc silicate phosphors must be
annealed to stabilize the coated phosphor. However, the
5 performance of a zinc silicate phosphor suffers both in
terms of brightness output and lumen maintenance after
annealing. Attempts to improve the base phosphor
performance prior to annealing include remilling and
refiring (RMF) the phosphor. Such an alumina coated "RMF"
10 phosphor shows improved lumen characteristics when used as
a component in the high color rendition triblend layer.
However, the remilling and refiring process results in a
large loss of starting material, thus increasing cost of
the phosphor. The present invention solves these problems
15 in a novel and economical way.

        In a related application, an improved compact fluores-
cent lamp can be manufactured using a coated willemite
phosphor as the green-emitting component. Compact
fluorescent lamps of the twin-tube and double twin-tube
20 variety have become important for energy conservation in
recent years since they have efficiencies which far exceed
those of conventional incandescent lamps. While these
lamps are very cost-effective with very short payback
periods, they, nevertheless, have high initial costs which
25 have limited the scope of applications in which they have
been exploited. Therefore, it is desirable to further
reduce the cost of these lamps through the use of less
expensive non-rare-earth-containing substitutes.

        The compact fluorescent lamps currently employ two
30 rare-earth based phosphors. They are Y_2O_3:Eu (Sylvania
Type 2342) for the red emission and Ce,Tb Mg Aluminate:
Ce, Tb (Sylvania Type 2293) for the green emission. No
blue-emitting phosphor is required, since the blue
components of the mercury discharge are used to achieve
35 the proper color temperature of the emitted 'white' light.
More recently, $LaPO_4$:Ce,Tb, manufactured by Nichia

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Corporation, is being considered as a replacement for the
Type 2293. Because these materials contain expensive
rare-earths as the activators, they are some of the most
expensive phosphors commercially used.

5   As mentioned previously, a green-emitting zinc ortho-
silicate phosphor activated with manganese, also known by
the mineral name willemite can be improved by the
application of a bi-layer coating prior to annealing. The
bi-layer consists of a thin coating of silica applied

10 between the base phosphor and a conformal alumina coating
which is exposed to the mercury discharge. The base
phosphor is a zinc silicate phosphor doped with manganese
and tungsten. This phosphor can be manufactured on
production scale equipment using a single step firing

15 procedure which provide very high yields (typically 90%).
These high yield and efficiencies of scale provide
substantial phosphor cost savings which far outweigh the
cost of applying the intermediate silica layer.

        Finally the use of the willemite phosphor which has
20 been coated with silica and then with alumina can be used
as the green-emitting component of high color rendition
fluorescent lamp.

        A method for forming a continuous layer of silica on
25 phosphor particles is disclosed. The method comprises
vaporizing a silicon containing precursor such as
tetramethyloxysilane (TMOS) or tetraethoxyorthosilane
(TEOS) into an inert carrier gas and passing this gas
containing TMOS or TEOS through a phosphor powder wherein

30 the phosphor particles are enveloped in the TMOS or TEOS
at a temperature of greater than 400°C. An oxidizing gas
is passed into the phosphor powder which reacts with the
TMOS to form a continuous coating of silica on the
phosphor particles. The resulting silica coated phosphor

35 can then be further coated with alumina.

In another aspect of the present invention, fluorescent lamps using the double coated bi-layer phosphor are manufactured. The resulting lamps show improved lumen and maintenance performance.

5   In yet another aspect of the present invention the double coated phosphor can be used in high color rendition fluorescent lamps. The bi-layer phosphor replaces the green emitting rare earth phosphors that are presently used in these lamps. The bi-layer phosphor results in a

10 less expensive lamp as the expensive green-emitting phosphor are replaced while the lamps suffers almost no loss in lumen output.

Some embodiments of the invention will now be

15 described, by way of example, with reference to the accompanying drawings in which:

FIGURE 1 is a schematic representation of an apparatus suitable for coating phosphor particles.

FIGURE 2 is a bed temperature versus time graph for a

20 TMOS/O_2 coating run using a manganese activated zinc silicate phosphor.

FIGURE 3 shows the weight percent of silica on phosphor powder as a function of coating time.

FIGURE 4 shows the relative plaque brightness versus

25 weight percent of silica coating on a zinc silicate phosphor.

FIGURE 5 shows a cross-sectional view of a phosphor particle coated with a layer of silica which is coated with a layer of alumina.

30   FIGURE 6 shows an elevational view of double coated fluorescent lamp.

FIGURE 7 shows a cross-sectional view of the lamp of Fig. 6.

FIGURE 8 shows the color points taken at 3 positions

35 of a double coated lamp using Type 2293 phosphor.

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FIGURE 9 shows the color points taken at 3 positions
of double coated lamp using an "RMF" phosphor.

FIGURE 10 shows the color points taken at positions of
a double coated lamp using the phosphor of the present
5 invention.

One aspect of the present invention involves the
formation of a continuous and conformal coating of silica
on the surfaces of zinc silicate or cool white phosphor
10 particles via chemical vapor deposition (CVD) while the
phosphor particles are suspended within an isothermal gas
fluidized bed. In a second aspect of the present
invention silica coatings are used to prevent reductions
in brightness and the development of body color when
15 manganese activated zinc silicate (Zn_2SiO_4:Mn) phosphors
are heated in air at temperatures above about 600°C.
These silica coatings also act as diffusion barriers, pre-
venting the migration of zinc and manganese from the
surface of the Zn_2SiO_4:Mn phosphor through the silica
20 coating and therefore also through continuous and
conformal alumina coatings that may be formed on the
surfaces of the silica coated phosphor particles.

A schematic representation of the fluidized bed
reactor used to coat the phosphor particles with silica is
25 shown in Fig. 1. In Fig. 1, a feeder line 11 carries the
inert bubbler gas through valve 54 into a stainless
bubbler 12 which contains a silicon containing precursor
such as tetramethoxysilane (TMOS) or tetraethoxyortho-
silane (TEOS). In the bubbler 12, the coating precursor,
30 TMOS or TEOS is vaporized into the bubbler gas. The
bubbler is heated by heating means such as heating tape
(not shown). The bubbler gas containing the TMOS or TEOS
can be diluted by carrier gas to provide appropriate
concentration of reactants. The bubbler gas containing
35 the vaporized TMOS or TEOS is carried through connector
line 13 and is diluted by the carrier gas at valve 55

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which is carried through line 111. Lines 13 and 111 join
and the resulting line is heated by heating tape 30 or
other means. The bubbler and carrier gas with the TMOS
passes through a stainless steel plenum 40 which is
5 maintained at a temperature of about 32°C. The carrier
gas along with the vaporized TMOS or TEOS then flows
through a porous stainless steel gas distributor 14. The
gas then flows into a quartz glass reaction tube 15.
Within the reaction tube 15 is a vibrating mixer 17.
10 Circumferentially located on the shaft of the vibrating
mixer 17 and near the vibrating disc 19 are a series of
holes 18 through which the oxidizing gas with or without
an inert diluting gas enters the reaction tube 15. Oxygen
is introduced to the reaction tube through line 21. No
15 diluting gas means for the oxygen is shown in Fig. 1. The
quartz glass reaction tube is surrounded by a furnace 20.

EXAMPLE 1
     Aluminum Oxide C (0.1%) was blended with each phosphor
20 as a fluidization aid. The temperature of the fluidized
bed reactor was maintained between 450°C and 460°C during
the coating process. Further, due to the moisture
produced within the high temperature fluidized bed as a
byproduct of the TMOS oxidation reaction, the fluidized
25 bed remained almost perfectly isothermal from the
beginning to the end of each coating process run. A
typical bed temperature versus time curve for a TMOS/O_2
coating run is shown in Figure 2. In a typical run, 400
mg of the phosphor are coated using a 32°C bubbler tem-
30 perature, with 0.5 1/min nitrogen gas (the fluidizing gas
medium) flowing through the TMOS bubbler, and with 0.6
1/min oxygen gas entering the fluidized powder bed
(through the hollow stirrer rod) at a point a few
centimeters above the level of the porous distributor
35 plate.

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Coating reactions were carried out for times ranging between 2.5 hours and 7.5 hours. Subsequently, the amounts of silica deposited were determined analytically for several of the coated phosphors. The results of these

5 determinations are listed in Table 1. These data are plotted vs coating time in Figure 3. As shown, the amount of silica deposited via the $TMOS/O_2$ coating reaction increases linearly with increasing coating time.

10   **TABLE 1**

Results of Chemical Analyses for Silica
Coatings on $TMOS/O_2$-Coated Zn_2SiO_4
and Cool White Phosphors*

15

Phosphor	Coating Time (hr)	Weight Percent SiO_2
Zn_2SiO_4	5	1.65
Cool White	2½	0.80
Cool White	5	1.77
Cool White	7½	2.56

20

*400 gm phosphors 0.5 l/min bubbler flow rate; 32°C bubbler temperature; 0.6 l/min O_2 flow rate; inert carrier gas for TMOS: N_2.

The silica-coated and uncoated zinc silicate and cool
25 white phosphors were also examined via high resolution scanning electron microscopy. Photographic images were obtained at 20,000X and 50,000X magnification. There were no features observed in the photomicrographs obtained with the silica-coated materials that were not observed in the
30 photomicrographs obtained with the corresponding uncoated phosphors. Thus, the silica coatings produced via the $TMOS/O_2$ reaction appear to be uniform and conformal to the surfaces of the underlying phosphor particles.

The continuity of the silica coatings formed on the
35 $ZnSiO_4$:Mn and cool-white phosphors were examined using X-ray photoelectron spectrometry. Typical normalized

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relative atomic concentration data obtained with an
uncoated and a silica-coated $ZnSiO_4$:Mn phosphor are
compared in Table 2. Typical data obtained with an
uncoated and a silica-coated cool white phosphor are
5   similarly compared in Table 3. As shown in Table 2,
signals corresponding to zinc and manganese are completely
absent from the XPS spectra obtained with the
$TMOS/O_2$-coated zinc silicate phosphor. Similarly, except
for a very small calcium signal, the XPS spectra obtained
10 with the $TMOS/O_2$-coated cool white phosphor contain no
evidence of the underlying phosphor. Thus, the silica
coatings formed upon the surfaces of the phosphor
particles appear to be continuous as well as conformal.

15   TABLE 2

Relative Atomic Concentrations of Surface
Elements from XPS Analyses of Uncoated and
Silica-Coated Zn_2SiO_4:Mn

Coating	Zn(3p)	Si(2p)	Mn(2p)
None	100	73	2
$\approx$ 2 w/o SiO_2 (from $TMOS/O_2$ reaction)	0	100	0

25

                                     TABLE 3

Relative Atomic Concentrations of Surface
Elements from XPS Analyses of Uncoated and
Silica-Coated Cool White Phosphor

Coating	Ca(2p)	F(1s)	P(2s)
None	100	23	63
$\approx$ 2 w/o SiO_2 (from $TMOS/O_2$ reaction)	<1	0	0

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EXAMPLE 2

Three different lots of Zn_2SiO_4:Mn phosphor were coated with silica according to the method described in Example 1. Samples of each phosphor, before and after
5 silica-coating, were annealed in air for 4 hours at 750°C. Additional samples were likewise annealed in the air for one hour at 800°C. Portions of each annealed material were pressed into so-called plaques (i.e., they were pressed into molds so that uniformly flat horizontal
10 surfaces were obtained.) A spot brightness meter equipped with a green photo-optic filter along with an unfiltered mercury plasma ultraviolet light source was used to measure a so-called plaque brightness for each sample, ex-pressed relative to that of a sample of each uncoated and
15 unannealed phosphor. The results of these measurements are listed in Table 4. The relative plaque brightnesses measured with phosphor lot #1 are also plotted vs w/o silica added during the TMOS/O_2-coating process in Figure 4.

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TABLE 4

Relative Plaque Brightness of TMOS/O_2-Coated Zn_2SiO_4:Mn*

Phosphor Lot	w/o SiO$_2$ Coating	Anneal Conditions	Relative Plaque Brightness (%)
1	0	none	100.0
		4 hr/750°C	95.6
		1½ hr/800°C	96.0
1	0.40	none	94.8
		4 hr/750°C	99.3
		1½ hr/800°C	100.4
1	0.80	none	86.9
		4 hr/750°C	99.3
		1½ hr/800°C	100.4
1	1.20	none	84.2
		4 hr/750°C	99.3
		1½ hr/800°C	100.4
2	0	none	100.0
		4 hr/750°C	95.9
		1½ hr/800°C	95.9
2	1.20	none	78.1
		1½ hr/800°C	100.3
3	0	none	100.0
		4 hr/750°C	95.7
		1½ hr/800°C	95.9
3	1.20	none	80.0
		1½ hr/800°C	101.9

*Bubbler Temp. = 32-33°C; Bubbler Flow Rate = 0.5 l/min; O_2 Flow Rate = 0.6 l/min; Powder Weight = 400 gm; Coating Temp = 450-460°C.

As shown, the brightness of the uncoated phosphor is lowered by at least 4% when annealed in the air at 750°C or at 800°C. A body color (corresponding to a reduction in reflected visible light) also develops during the annealing of the uncoated phosphor. On the other hand, sizable reductions in brightness are also observed with the unannealed silica-coated phosphors. Moreover, the thicker the silica coating, the lower the measured plaque brightness. For instance, the plaque brightness measured

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with a zinc silicate phosphor coated with 1.20 w/o silica
(via the TMOS/O_2 reaction) is only around 80% of that
measured with the uncoated phosphor.

In contrast, plaque brightnesses nearly equal to or
5   exceeding those measured with the uncoated and unannealed
phosphor are obtained with silica-coated phosphors that
have been annealed in the air at temperatures between
750°C and 800°C. Such silica-coated and annealed
materials are also notable for an absence of the body-
10 color that develops during the annealing of the uncoated
phosphor. Therefore, whereas the uncoated phosphor cannot
be air-annealed without suffering a 4% - 5% reduction in
plaque brightness as well as a reduction in reflected
visible light, the brightness of a silica-coated phosphor
15 actually increases with increasing annealing temperature
to a level exceeding that measured with the uncoated and
unannealed phosphor, itself.

EXAMPLE 3
20   The implication of the data shown in Example 2 is that
detrimental interactions which normally occur between the
phosphor and the air during the annealing step are
prevented when the phosphor is coated with a thin layer of
silica. The body-color that develops during the annealing
25 of the uncoated Zn_2SiO_4:Mn phosphor suggests that the Mn^{2+}
ions located on or near to the phosphor particle surface
are oxidized during the anneal. However, it is possible
that the body color is due to oxidized tungsten at the
phosphor particle surface. The absence of this
30 undesirable body-color, the undiminished brightnesses
obtained with annealed silica-coated Zn_2SiO_4:Mn phosphors,
and the observed continuity and conformality of the silica
coatings themselves indicate that the phosphor surface is
stabilized by the presence of the coating, thereby
35 preventing the surface manganese from interacting with the
oxidizing atmosphere within the annealing furnace.

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That the phosphor surface is stabilized by the presence of the silica coating may also be shown by examining the coated phosphor using x-ray photoelectron spectrometry. Listed in Table 5 are the normalized

5　relative atomic concentrations of Al, Zn, Si, and Mn obtained with several samples from the measured XPS signal intensities corresponding to the Al(2p), Zn(3p), Si(2p), and Mn(2p) electrons, respectively. Sample 1 is a Zn_2SiO_4:Mn phosphor coated with alumina using aluminum

10　isopropoxide (AIP) as the organometallic coating precursor. The AIP is vaporized into an inert carrier gas and passed through a mixture of the phosphor powder and up to 1 percent of a fluidizing aid to form an isothermal fluidized bed of vaporized AIP and phosphor particles at a

15　temperature of 300°C or greater. Oxygen is passed into the fluidized bed and reacted with the vaporized AIP to form alumina on the outer surfaces of the phosphor particles. Sample 3 was obtained by coating the same phosphor with silica as described in Example 1 (using TMOS

20　as the coating precursor). Samples 2 and 4 were obtained by air-annealing samples 1 and 3, respectively, for 4 hours at 750°C.

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TABLE 5

Relative Atomic Concentrations for XPS Analyses
AIP/O$_2$-Coated, TMOS/O$_2$-Coated, and
TMOS/O$_2$ AIP/O$_2$-Coated Zn$_2$SiO$_4$:Mn

Sample No.	Material	Al(2p)	Zn(3p)	Si(2p)	Mn(2p)
1	AIP/O$_2$-Coated [a] Zn$_2$SiO$_4$	100	0	0	0
2	Sample 1, annealed 4 hr 750°C	100	13	0	3
3	TMOS/O$_2$-Coated [b] Zn$_2$SiO$_4$	0	0	100	0
4	Sample 3, annealed 4 hr 750°C	0	0	100	0
5	Sample 4, AIP-O$_2$- [a,b] Coated	100	0	0	0
6	Sample 5, annealed 4 hr 750°C	100	0	0	0

a = 2% Al$_2$O$_3$ Coating
b = 2% SiO$_2$ Coating

As shown in Table 5, none of the cations present in the Zn$_2$SiO$_4$:Mn phosphor are detected in the XPS spectra obtained with the alumina-coated phosphor. This indicates that the AIP/O$_2$ coating is continuous and thick enough to filter any Zn(3p), Si(2p), or Mn(2p) electrons that might be emitted under x-ray bombardment. In contrast, relatively large Zn(3p) and Mn(2p) signals are detected after annealing the alumina-coated phosphor for 4 hours at 750°C (sample 2). These results are interpreted to indicate that these cations are mobile enough to migrate through the alumina coating during the anneal. In sharp contrast are the XPS data obtained with the TMOS/O$_2$-coated samples. In this case, silicon is the only cationic species detected either before or after the 4 hour 750°C anneal, indicating that the zinc and manganese ions present on the surface of the Zn$_2$SiO$_4$:Mn phosphor do not migrate through the silica coating during the anneal. The

fact that the alumina-coated phosphor possesses a distinct
body-color after the anneal (thought to be due to oxidized
manganese), whereas the annealed silica-coated phosphor
does not possess such a body-color can be understood from
5 these data.

Finally, consider the results obtained using the
Zn_2SiO_4:Mn phosphor that has been silica-coated via the
$TMOS/O_2$ reaction and subsequently air-annealed for 4 hours
at 750°C (sample 4). A quantity of this silica-coated and
10 annealed phosphor was coated with alumina via the AIP/O_2
reaction as described previously. As shown in Table 5
(sample 5), Al is the only cationic species detected via
XPS analysis of this material, indicating that the alumina
coating is continuous and uniformly thick enough to
15 prevent the detection of any Si(2p) electrons that might
be generated under x-ray bombardment. Most significant is
the fact that an identical result is obtained after
annealing the double-coated phosphor for 4 hours at 750°C.
In contrast to the results obtained with sample 2 (in the
20 absence of the silica diffusion barrier), the absence of
XPS signals indicating the presence of Zn, Si, or Mn near
to the surface of the annealed double-coated material and
the complete absence of any detectable body-color
indicates that the silica coating prevents the interaction
25 between the phosphor and the alumina coating that would
otherwise occur.

This conclusion is reinforced by the relative plaque
brightness data listed in Table 6. Shown are the measured
brightnesses (relative to that of the uncoated and
30 unannealed phosphor) of AIP/O_2-coated Zn_2SiO_4:Mn before
and after a 4 hour 750°C anneal, both with and without a
$TMOS/O_2$ (silica) diffusion barrier. As indicated in the
table, the reduction in brightness observed with the
unannealed phosphor in the absence of the diffusion
35 barrier is more than twice that obtained with the
double-coated phosphor. More significantly, the reduction

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in brightness observed with the annealed alumina-coated
phosphor in the absence of the diffusion barrier is an
order of magnitude greater than that obtained when the
alumina coating was applied over the diffusion barrier.
5 Thus, the plaque brightness measured with the
double-coated and annealed phosphor was only about 1%
below that measured with the virgin phosphor.

TABLE 6

10

Relative Plaque Brightnesses of AIP/O_2-Coated
Zn_2SiO_4:Mn with and without underlying
SiO_2 Diffusion Barrier[1]

15 w/o SiO_2[2] Coating	Anneal Conditions	Plaque Brightness Relative[3] to that of Uncoated Phosphor
0	none	94.2%
	4 hr/750°C	87.7%
20		
1.20	none	97.3%
	4 hr/750°C	98.8%

25 [1] Ca. 2 w/o Al_2O_3 Coating

[2] SiO_2-coated phosphor was annealed 4 hours at 750°C
prior to coating with alumina

[3] Plaque brightnesses relative to that measured with the
uncoated phosphor.

30   Due to the results obtained from Examples 1-3 it was
thought that the results of improved plaque brightness and
lumen maintenance could be extended to fluorescent lamps.
However, it is known that correlation between handlamp
plaque brightness and fluorescent lamp performance for a
35 given phosphor frequently do not exist. This results from
a multitude of factors including changes in the phosphor

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which occur during lamp baking, lamp fabrication and the
contact of the phosphor with the mercury discharge.
Moreover, the mercury discharge within a fluorescent lamp
contains about 15% of its emission at 185 nm. This
5 short-wavelength emission can lead to enhanced brightness
and/or damage to the phosphor which can influence the
observed initial brightness and maintenance.

More specifically, in the case of the alumina coated
and annealed willemite phosphor, the fluorescent lamps
10 which have the highest lumen performance possess a plaque
brightness of 92% of the virgin phosphor. However, the
corresponding fluorescent lamp performance may only be a
few percent lower.   Further, while the handlamp
photoluminescent performance is improved with a silica
15 coated and annealed phosphor, this material exhibits a
significant loss in brightness and catastrophic
maintenance loss within a fluorescent lamp. This behavior
is probably associated with the reaction of the phosphor
with the mercury discharge within the fluorescent lamp.
20   Shown in Fig. 5 is a cross-sectional view of a
phosphor particle coated with a bi-layer. The phosphor
grain is coated with a silica layer which prevents
diffusion from the phosphor grain to the surface coating
of alumina. It is also believed that the silica layer
25 prevents diffusion of the alumina layer to the phosphor
grain. Potential uses of the phosphor shown in Fig. 5 are
discussed below.

Historically silica and silica-containing phosphors
used within fluorescent lamps are known to give rise to
30 appreciable maintenance loss, the uncoated willemite, in
fact, being a prime example of this. Therefore, any
improvement due to a protective layer over a silica
coating can be expected to be strongly dependent on the
quality and conformality of that layer as well as the
35 intrinsic resistance of the specific phosphor to
degradation in a fluorescent lamp.

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EXAMPLE 4

Silica coatings were applied to the surfaces of zinc silicate phosphors by CVD in a fluidized bed described in Example 1. However, the tests were carried out using

5   typically 1500 gms. of phosphor in an 80 mm ID quartz tube which employed a quartz frit as the distributor. Aluminum Oxide C was blended with the phosphor at a concentration of 0.1% by weight of the fluidized bed reactor was maintained between 450 and 460°C during the coating

10 process. This temperature was monitored by a thermocouple placed within the bed located at the midbed height. In a typical run 2 liters per minute were run through a bubbler containing tetramethoxyorthosilicate (TMOS) liquid maintained at 32°C, and 3 liters per minute of undiluted

15 oxygen entered the bed through a hollow stirrer rod which was located a few centimeters above the level of the porous distributor plate. Coating reactions were carried out between 1½ hrs. and 5 hrs. to effect the deposition of predetermined amounts of silica coating. Table 7

20 summarizes the powder properties of the virgin phosphors used in the following examples.

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TABLE 7

Particle Properties of the Virgin Zinc Silicate
Phosphors Used in the Examples Cited

Lot No.	Surface Area (M^2/gm) [1]	FSS (Fisher Sieve Size, microns)	Coulter Counter Particle Size (sonic) [2]	
			50%	O.D. [3]
66RMF	0.38	6.7	9.0	0.23
TK1-2M	0.44	6.1	7.72	0.26
TK2-U	0.52	5.1	6.65	0.27

[1] Determined by single-point BET measurements, using a Quantachrome Monosorb surface area instrument.

[2] Based on volume.

[3] Q.D. is defined as $(d_{75\%}-d_{25\%})/(d_{75\%}+d_{25\%})$, and is a relative measure of breadth in the particle distribution.

Following coating, the phosphors were annealed in quartz boats for about 4 hours at an annealing temperature of approximately 760°C. At this point phosphors were coated with alumina as described below.

The CVD coatings were carried out on the annealed phosphors described above in a fluidized bed using trimethyl aluminum (TMA) and oxygen as precursors. The equipment and procedures for fluidized bed coating of willemite phosphors are described in detail in U.S. Patent No. 4,950,948. Briefly, a blend of approximately 1000 to 1300 gms. and 0.1% of Aluminum Oxide C by weight of phosphor was loaded into a quartz fluidized bed column comprising an 80 mm ID quartz tube having a quartz frit fused to the bottom which acted as the distributor plate. A 65 mm stainless steel agitator disc was attached to a vibromixer agitator. Approximately 5 cm from the base, a

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two-micron stainless steel filter element was welded in
line and functioned as a diffuser of the oxygen mixture.
The agitator disc itself was located approximately 25 mm
above the quartz distributor. A thermocouple, located at
5 the midbed height within the fluidized bed, was used to
monitor the temperature of the bed, which was maintained
between approximately 420 and 450°C.

The apparatus used for carrying out the coating reac-
tions is shown in Fig. 1 with some slight alterations. In
10 a typical run, which lasted between 3 and 5 hours, 1750 cc
per minute of nitrogen passed through a bubbler 12
containing trimethyl aluminum (TMA) liquid which was main-
tained at 30°C. Another 1250 cc per minute of nitrogen
carrier gas was used to dilute the flow through line 111.
15 The combined flow was used to fluidize the phosphor
particles in reaction vessel 15. The oxygen as an
oxygen/inert gas mixture was introduced through line 21 at
2500 cc per minute of oxygen and 50 cc per minute of
nitrogen into the fluidized bed through the two-micron
20 filter element described earlier. Table 8 summarizes
specific coating parameters used for the examples cited.

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TABLE 8

Coating parameters used to apply Al_2O_3 and SiO_2 layers to the zinc silicate phosphors described in this disclosure.

No.	Sample No.	Run No.	Bed Loading	Bubbler O₂	Coating Time	Run No.	Bed Loading	Bubbler	Carrier	O₂	Coating Time	SiO_2 Wt%	SiO_2 Thickness	Al_2O_3 Wt%	Al_2O_3 Thickness
6RNFF	#385	----- No silica -----				CNM120-89	2000 gms	1750cc	1250cc	2500cc	5 hrs.			2.28%	150Å
	#441	TMOS-29L	1500 gms	2 L/min	3½ hrs.	CNM330-89	1230 gms	1750cc	1250cc	2500cc	3 hrs.	1.26%	144Å	2.22%	147Å
k1-2M	#518	----No silica----				CNM1017-89	1500 gms	1750cc	1250cc	2500cc	4-1/3 hrs.				150Å
	#479	TMOS-38L	1500 gms	2 L/min	1½ hrs.	CNM614-89	1295 gms	1750cc	1250cc	2500cc	4½ hrs.	0.81%	80Å	2.65%	150Å
	#476	TMOS-37L	1500 gms	2 L/min	5 hrs.	CNM612-89	1070 gms	1750cc	1250cc	2500cc	3½ hrs.	1.80%	178Å	2.62%	150Å
k2-U	#425	----No silica----				CNM313-89	350 gms+	400cc	350cc	500cc	4 hrs.				115Å
	#443	TMOS-30L	1500 gms	2 L/min	5 hrs.	CNM403-89	1120 gms	1750cc	1250cc	2500cc	3-5/6 hrs.	1.80%	150Å	3.12%	150Å

+ This run was carried out in a 40mm I.D. quartz column; earlier data has shown equivalence between the small (40mm) and large (80mm) column runs. Also, no performance differences have been seen between 100-300Å Al_2O_3-only coated willemite phosphors.

Values for the thickness are derived from the weight percent SiO_2 or Al_2O_3 deposited and an assumed density of 2.3gms/cc and 3.97gms/cc, respectively.

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Once the phosphor particles were coated, they were
transferred to quartz boats and annealed at approximately
760°C for 4 hours.

5 Lamp Testing

After the annealing step described above, the
phosphors were coated in 20WT12 or 30 WT12 fluorescent
lamps using conventional water base suspension systems.
The lamps thus coated were processed into finished
10 fluorescent lamps and photometrically evaluated. The data
were then converted to corresponding 40WT12 data using
established correction factors.

In the tests cited below, the bilayer coated and an-
nealed phosphors were tested against Sylvania Type 2293,
15 which is a Ce,Tb, Mg Aluminate phosphor used as a
green-emitting component in high color rendition lamps.
In addition, the uncoated virgin phosphor and the singly
coated and annealed (i.e., alumina only) phosphors were
also evaluated with the test.

20   Table 9 lists the lifetest results of the phosphors.
It is clearly evident that the bilayer coating provides
0-hr. brightness values which are either equivalent to or
exceeds that of the virgin phosphor lot. Also, both the
single- and bilayer-coated phosphors possess maintenance
25 which significantly exceeds the virgin phosphor. However,
the bilayer (Al_2O_3/SiO_2) annealed phosphor substantially
exceeds the brightness of the Al_2O_3-only phosphor by 8%
for the 'RMF' phosphor (66RMF) to as much as 17% for the
singly fired willemite phosphors (TK1-2M and TK2-U lots).
30 Note that the brightness observed for the alumina-only
coated and annealed singly fired willemite phosphor lots
are so low as to eliminate their consideration for
commercial use in conventional high color rendition lamps,
whereas the substantially higher brightness of the
35 Al_2O_3/SiO_2 coated singly fired phosphor allows its use in

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triblend lamps. The thickness of the silica coatings are derived from the information shown in Table 8.

TABLE 9

Lifetest Data for Various Willemite Phosphor

66RMF Lot

	O hr	100 hr	% M(0-100)	500 hr	%M(0-500)
Virgin	5329	3800	71.3	--Discontinued--	
#385 Al_2O_3	4860	4763	98.0	4685	96.4
#441 Al_2O_3/ SiO_2 FHX164	5245	5101	97.3	5048	96.2
Type 2293	4923	4768	96.8	4685	95.2

TK1-2M Lot

	O hr	100 hr	% M(0-100)	500 hr	%M(0-500)
Virgin	5199	---	---	---	---
#578+ Al_2O_3	4491	4424	98.5	---	---
#479 Al_2O_3/ SiO_2(80Å)	5219	5193	99.5	4887	93.6
#476 Al_2O_3/ SiO_2(178Å)	5239	5137	98.0	4894	93.4
FHX343 Type 2293	4873	4757	97.6	4499	92.3

+ This sample was run in a separate test against Type 2293 Lot FHX343. In that test FHX343 gave O hrs = 4903 l, 100 hrs = 4736 l, (0-100%M=96.6%). Therefore, the major conclusions put forth are not affected.

TK2-U Lot

	O hr	100 hr	% M(0-100)	500 hr	%M(0-500)
Virgin	5021	---	---	---	---
#425 Al_2O_3	4499	4332	96.3	4264	84.7
#443 Al_2O_3/ SiO_2 FHX164	5084	4878	95.9	4842	95.2
Type 2293	4923	4768	96.8	4685	95.2

Note that values given have been corrected from corresponding 20WT12 and 30WT12 to 40WT12 fluorescent lamp data using established correction factors. Test Samples for lots 66RMF and TK2-U were evaluated in 20WT12 lamps; Lot TK1-2M was evaluated in 30WT12 lamps.

As mentioned earlier, the singly fired phosphor can be manufactured on a production scale with much higher yields than can be obtained using the 'RMF' synthesis.

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The much higher yields and efficiencies of scale favor
substantial cost savings.

It is important to note that the addition of the
silica interface provides a major improvement in the
5 100-hr. brightness, as well, over the alumina coatings
alone. As the data in Table 9 show, Sample #479 has
yielded a 100-hour brightness of 5193 lumens. This
corresponds to the highest value ever achieved for a
willemite phosphor after 100 hours of burning corrected to
10 equivalent 40WT12 fluorescent lamp performance. This has
significant commercial implications since published
ratings of 'initial brightness' are actually those
determined after 100 hours of lamp operation.

When tricomponent blend suspensions are used which
15 consist of Y_2O_3:Eu for the red emission, Ba,Mg
Aluminate:Eu for the blue emission, and the 'RMF' coated
and annealed phosphor described by U.S. Patent No.
4,925,703 for the green emission, a color variation in the
emitted light is observed from the fluorescent lamp across
20 its length manifested by a slightly red coloration on the
more thinly coated end of the lamp and slightly green
coloration on the more thickly coated end of the
fluorescent lamp. This end-to-end color variation is
believed to be due, in part, to the disparity in particle
25 size between the red and green phosphors in the suspension
used to make the coated lamps. In fact, lamp fabrication
using Sample #443, a bilayer coated and annealed TK2-U lot
of smaller particle size than the 'RMF' phosphor, showed a
significant reduction in color nonuniformity compared to a
30 coated and annealed 66RMF phosphor (Sample #441) run in
the same test. Thus, the bilayer coating allows <u>particle
size reduction while maintaining excellent brightness for
high color rendition triblend applications.</u>

Table 10 lists the x-ray photoelectron spectroscopy
35 (XPS) analyses of the surfaces after each of the stages of
processing leading to the alumina only and alumina/silica

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coated and annealed phosphors. The data clearly show that
the silica layer either eliminates or substantially
reduces the migration of Zn and Mn through the alumina
coating. It is also expected, although not experimentally
5 verified, that the silica interfacial layer also prevents
the migration of Al ions from the alumina coating into the
zinc silicate phosphor. Both factors contribute to the
elimination of undesirable light-absorbing body color of
the annealed phosphor and the interference from impurities
10 that lead to the loss in generation of efficient
luminescence.

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TABLE 10
X-ray Photoelectron Spectroscopy Analyses of Coated Willemite Phosphors

Sample Designation	Sl	Al	O	Atomic Percent Zn	Mn	C
66 RMF Virgin Powder	15.8	--	54.6	22.3	0.7	6.6
CWM 120-89 (TMA coated)	--	43.4	51.6	<0.1	--	4.9
#385 (TMA coated/annealed)	--	42.0	52.5	4.3	0.2	1.1
TMOS 29L (Silica coated)	38.5	--	58.8	1.1	--	1.4
#439 (Silica coated/annealed)	39.0	--	58.2	--	--	2.8
CWM 330-89 (TMA coated #439)	--	44.1	51.6	--		4.3
#441 (CWM 330-89/annealed)	--	45.2	51.3	0.2	--	3.2
TK-2U Virgin phosphor	16.0	--	48.6	17.7	0.9	16.0
CWM 313-89 (TMA coated)	--	43.7	52.8	--	--	3.5
#425 (TMA coated/annealed)	--	36.9	45.8	10.1	0.4	6.6
TMOS 30L (Silica coated)	36.4	--	56.1	0.2	--	7.3
#440 (Silica coated/annealed)	37.2	--	53.9	<0.1	--	8.8
CWM 403-89 (TMA coated #440)	--	43.6	52.8	--	--	3.6
#443 (CWM 403-89 annealed)	--	45.4	50.4	<0.1	--	4.2
TK1-2M Virgin phosphor	13.3	--	44.1	27.7	0.5	14.3
TMOS 38L (Silica coated)	38.1	--	60.4	<0.1	--	1.5
#477 (Silica coated/anneal)	37.7	--	59.8	<0.1	--	2.4
CWM 614-89 (TMA coated #477)	--	42.5	53.1	--	--	4.4
#479 (CWM 614-89 Annealed)	--	45.1	51.8	<0.1	--	3.0

Lamp tests carried out employing the single-coated alumina 'RMF' zinc silicate phosphor produced by the Chemical and Metallurgical Division of GTE Products Corporation, Towanda, PA, have shown a lower brightness

level in tri-phosphor blends when compared with the
rare-earth-containing blends run in the same test (See
Table 11). A bilayer (Al_2O_3/SiO_2) coated willemite
described employing a single-step fired willemite base
5   material in 40WT12 fluorescent lamps (Sample #541) has
yielded performance of 5280 lumens at 0 hours of lamp
operation and 5144 lumens at 100 hours with a maintenance
of 97.4% which exceeds that of the Type 2293 by almost 1%.
This performance substantially exceeds that obtained with
10 the best alumina-coated "RMF" materials heretofore
available. (See Table 11 for single- component life test
data) Thus, it is probable that this substantially less
expensive silica/alumina coated single-step fired
willemite phosphor is useful as single components and as
15 components of blends in double twin-tube lamps. This
phosphor will replace the more expensive Sylvania Type
2293 and the Nichia $LaPO_4$:Ce, Tb phosphors presently used.
Further uses for the silica/alumina coated phosphors are
discussed below.

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TABLE 11

Lifetest data for lamps containing alumina-coated 'RMF' willemite and rare-earth green tri-phosphor blends.*

Single-Coat Lamps: 20WT12, 3500°K

Green Test Sample	P.Wt. (gms)	X	Y	Lumens 0 Hr	Lumens 100 Hr	(0-100 Hr)%M
Control						
2293	1.95	0.410	0.398	1433	1389	96.9
G077						
(Willemite)	1.85	0.408	0.397	1354	1308	96.6
Delta Lumens				-79	-81	
Delta Percent				-5.5%	-5.8%	

Double-Coat Lamps: 20WT12, D35 (Designer, 3500°K)

Green Test Sample	Second Coat P.Wt. (gms)	X	Y	Lumens 0 Hr	Lumens 100 Hr	(0-100 Hr)%M
Control 2293	0.52	0.412	0.400	1353	1339	99.0
G077						
(Willemite)	0.55	0.412	0.398	1314	1291	98.2
Delta Lumens				-39	-48	
Delta Percent				-2.9%	-3.6%	

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*Lifetest data for single components in 40WT12 fluorescent lamps are:

	0 Hr	100 Hr	(0-100 Hr)%M
Control 2293	4921	4740	96.3
G077 (60 RMF)	5019	4695	93.5
Virgin 60RMF(uncoated)	5134	4143	80.7

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Referring to Figs. 6 and 7, there is shown in Fig. 6 and arc discharge lamp of the fluorescent type. The lamp 10 is comprised of an elongated glass tube 12 of circular cross-section. It has the usual electrodes 14 and 16 at
5   each end supported by lead-in wires, 18, 20 and 22, 24, respectively, which extend through glass presses 26, 28 in mount stems 30, 32 to the contacts in bases 34, 36 affixed to the ends of the lamp.

The sealed tube is filled with an inert gas such as
10 Argon or a mixture of Argon and Krypton at a low pressure, for example 2 torr, and a small quantity of mercury, at least enough to provide a low vapor pressure during operation.

The interior of tube 12 is coated with a first layer
15 of phosphor 38 such as, for example, a calcium halophosphate activated by antimony and manganese.

A phosphor coating suspension was prepared by dispersing the phosphor particles in a water-based system employing polyethylene oxide and hydroxyethyl cellulose as
20 the binders with water as the solvent.

The phosphor suspension was applied in the usual manner of causing the suspension to flow down the inner surface of the bulb and allowing the water to evaporate leaving the binder and phosphor particles adhered to the
25 bulb wall.

The first layer 38 was then dried prior to overcoating with a second phosphor layer 40 comprised of narrow-band red- and blue- emitting phosphors and a broad-band green-emitting phosphor. These two narrow-band
30 phosphors can be, for example, a yttrium oxide activated by trivalent europium and having a peak emission at 611 nm; and barium magnesium aluminate activated by divalent europium and having a peak emission at 455 nm. The broader band phosphor was alumina/ silica-coated zinc
35 silicate activated by manganese and having a peak emission at 528 nm.

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The second phosphor layer containing the CVD-coated phosphor is applied from a water-based suspension by allowing the coating to flow down over the first phosphor layer 38 until the phosphor coating drained from the

5   bottom of the bulb indicating the coverage of the phosphor layer 38 was complete. Lamps made by this method usually exhibit the thinnest coating thickness on the top end of the bulb and the heaviest thickness on the bottom end, where the suspension is allowed to drain. The

10   double-coated bulbs were then baked and processed into fluorescent lamps by conventional techniques.

In the case where only a single layer lamp was made, the methods were essentially the same as described herein with the exception that the halophosphate layer was not

15   applied.

Control lamps were fabricated by identical techniques as described above but had a narrow-band green-emitting magnesium aluminate phosphor activated by cerium and terbium in the second phosphor layer with a

20   peak emission at 545 nm. This phosphor is generally used in the tri-phosphor blend but was replaced by the green CVD-coated willemite phosphor in this invention.

Lamps employing a representative alumina-only coated and annealed 'RMF' willemite phosphor, manufactured by the

25   Chemical and Metallurgical Division of PMG, Towanda, PA, were also fabricated and incorporated into the testing.

Lifetest data and particle size information for the single component willemite phosphors used for the tri-phosphor blend lamps are given in Tables 12 and 13,

30   respectively. These values have been corrected to obtain the performance levels that would be observed with 40T12 fluorescent lamps using established correction factors.

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TABLE 12

Lifetest data for single-component fluorescent lamps con-
taining coated willemite phosphors (corrected to 40WT12)

	0 Hr	100 Hr	500 Hr	%M(0-500 Hr)
Type 2293 (control)	4923	4768	4685	95.2
#425 (TK2-U)+	4499	4332	4264	94.7
#443 (TK2-U)++	5084	4878	4842	95.2
G103 (61RMF)+	5085	4804	4677	92.0
#441 (66RMF)++	5245	5101	5048	96.2

+ Phosphor grains coated with only a single coating of
   alumina, (sample G103 was prepared at Chem. and Met.
Div.
   PMG, Towanda, PA).

++ Phosphor grains coated with both silica and alumina.

TABLE 13

Particle properties of the virgin zinc silicate
phosphors used in the examples cited.

Lot Number	FSS (Fisher Sieve Size, microns)	Coulter Counter Particle Size (sonic)	
		50%	Q.D.
Singly Fired TK-U	5.1	6.7	0.27
'RMF'			
60 RMF	7.4	9.3	0.21
61 RMF	8.0	10.0	0.21
66 RMF	6.7	9.0	0.23

For the evaluation of the tri-blends containing the
alumina/silica-coated willemite phosphor, two different
lamp types were used, and compared with controls which did
not have this phosphor in the blend. The lamps were
tested by photometering for light output in a standard
photometric sphere, both initially and at stated times.
In the following tables, light outputs are expressed in

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lumens. Lamp color values were obtained by spectral power
distribution (SPD) measurements.

EXAMPLE 5

5   This example compares the light output and
maintenance of alumina/silica-coated and annealed
willemite phosphors in the tri-phosphor blends for double
layered 96-inch Designer 3000°K High Output Super Saver
fluorescent lamps. This lamp type has a tri-phosphor
10   weight in the second layer of about 15% of the total
phosphor in the two layers. The lamps were fabricated to
obtain the same x and y color coordinates for both the
test and control by adjusting the tri-phosphor blend
composition. The lamp test results are listed in Table
15   14. As the test data show, the lumens and lumen
maintenance of the test group are equivalent to the
rare-earth-containing Type 2293 control. This is in
contrast to previous results obtained with alumina-only
(single-coated and annealed) 'RMF' phosphor where Designer
20   lamp brightness values were typically 3% to 4% lower than
those obtained with the standard tri-phosphor blend (see
Table 11 for comparison).

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TABLE 14

Lifetest data for double-coat lamps where the triblends contain rare-earth green-emitting phosphor and two Al_2O_3/SiO_2-coated willemite phosphors.

Lamp Type: 96T12/D30/HO/SS (Designer, 3000°K, high output, supersaver)

Green Component Test Sample	Phosphor	Composition-Second Layer Tri-Phosphor (Weight %)[+](1)			Tri-Phosphor Weight(Grams)	Color Coordinates	
		Red(Y_2O_3:Eu)	Green	Blue(Ba,MgAlO:Eu)		X	Y
Control 2293	(Ce,Tb)MgAlO:Ce,Tb	65.8	31.3	2.9	1.84	0.429	0.410
#441(66RMF)	Zn_2SiO_4:Mn,W'RMF'*	66.7	30.8	2.5	1.90	0.435	0.405
#443(TK2-U)	Zn_2SiO_4:Mn,W Single Fired	66.1	31.4	2.5	1.92	0.434	0.403

+ First layer is a holophosphate phosphor Sylvania Type 4300 with color coordinates in finished lamp of X=0.440, Y=0.405; first layer weight = 11-12 gms.

* Alumina/silica coated

Photo Metric Results

	Lumens 0 Hour	Lumens 100 Hours	Lumens 500 Hours	Lumen Maintenance % 0-500 Hours
Control 2293	8753	8573	8060	92.1
#441	8763	8430	8082	92.2
#443	8765	8368	8063	92.0

(1) Red component is Sylvania Type 2345 (Y_2O_3:Eu); Blue component is Sylvania Type 246 (Ba,MgAlO:Eu)

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EXAMPLE 6

    As mentioned earlier, color nonuniformities of
fluorescent lamps containing the 'RMF' coated and annealed
phosphor occur and become more severe as the bulb length

5 increases. The 96-inch lamps have shown the most
pronounced variation. Color nonuniformities strongly
influence consumer acceptance of the lamp since they are a
premium-priced product designed for use in high color
rendition applications.

10   Figs. 8 through 10 show the color points taken from
the more heavily coated end (HE), middle (M), and more
lightly coated end (LE) of the fluorescent lamp containing
the rare earth green, the bilayer-coated 'RMF' phosphor
(#441), and the bilayer-coated single-fired willemite

15 phosphor (#443), respectively. Also shown are the two-
and three-step Macadam ellipses. The Macadam ellipse is a
way of assessing differences in visual color perception.
For acceptable lamps it is desirable to have all points
residing well within the two-step ellipse. As shown in

20 Fig. 8, the end-to-end color variation is excellent in the
case of the rare-earth green Type 2293. However, the
'RMF'-based phosphor shows a red and green variation along
the length of the lamp, as shown in Fig. 9. In contrast,
as shown in Fig. 10, the singly fired phosphor (Sample

25 #443) shows a significant improvement in color uniformity
over the 'RMF' phosphor, well within acceptable limits.
It is thought that the color non-uniformity originates
from a particle-size disparity between the red and green
phosphors that make up the dispersion from which the lamps

30 are made. Thus, <u>the bilayer coating allows particle size
reduction of the green component while maintaining
excellent brightness for high color rendition
applications</u>. (As shown in Table 12, the fluorescent lamp
brightness obtained with the alumina/silica-coated small

35 particle phosphor (Sample #443) is much superior to that

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obtained with the same base phosphor coated only with
alumina (Sample #425)).

EXAMPLE 7

5   This example compares the light output and
maintenance of alumina-coated and alumina/silica-coated
willemite phosphors in 40WT12 4100°K single-coat
tri-phosphor lamps. This test is designed to exaggerate
differences in performances between the green components
10 used in the triblends, since the single layer of high
color temperature requires the largest amount of green
compared to any other lamp that would be fabricated. That
is, any differences in performance will diminish as the
triblend layer thickness is reduced (in double layer
15 lamps) and as the lamp color temperature is reduced (since
the fraction of green component in the blend goes down as
the color temperature is reduced).

      As the data in Table 15 show, the maintenance of all
materials tested are comparable. Further, the color
20 rendering index, measured after 100 hours of lamp
operation, is about 3 units higher for the
willemite-containing blends compared to the
rare-earth-containing blend, even in this single-coat
lamp, achieving CRI values in excess of 85.

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TABLE 15

Lifetest data for triblends containing rare-earth green-emitting green phosphor, alumina-coated willemites, and Al_2O_3/SiO_2-coated willemite phosphor.

Lamp Type: 40T12/4100°K/single-coat triphosphor (no halo layer)

Green Component Test Sample	Phosphor	Composition-Second Layer Tri-Phosphor (Weight %)* Red(Y_2O_3:Eu)	Blue(Ba,MgAlO:Eu)	Green	Tri-Phosphor Weight(Grams)	Color Coordinates X	Y	CRI 100 Hours
Control 2293	(Ce,Tb)MgAlO:Ce,Tb	48.0	10.3	41.6	3.31	0.376	0.385	82.5
G103(61RMF)**	Zn_2SiO_4:Mn,W RMF Al_2O_3 only	51.4	11.4	37.2	3.85	0.376	0.385	85.6
#441(66RMF)***	Zn_2SiO_4:Mn,W RMF	54.8	11.6	33.6	4.07	0.380	0.389	85.3
#4431(TK2-U)***	Zn_2SiO_4:Mn,W Single Fired	53.1	12.6	34.3	3.74	0.378	0.388	85.4

* Red component is Sylvania Type 2345 (Y_2O_3:Eu); Blue component is Sylvania Type 246 (Ba,MgAlO:Eu)

** Manufactured at Chemical & Metallurgical Division, PMG, Towanda, PA (Alumina-coated willemite phosphor)

*** Alumina/Silica-coated willemite phosphor.

Photo Metric Results

	Lumens 0 Hour	Lumens 100 Hours	Lumens 500 Hours	Lumens 1000 Hours	Lumen Maintenance % 0-1000 Hours
Control 2293	3427	3319	3252	3161	92.2
G103(61RMF)	3341	3183	3080	3006	90.0
#441(66RMF)	3421	3291	3215	3176	92.8
#4431(TK2-U)	3364	3233	3147	3095	92.0

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With regard to brightness, the bilayer-coated 'RMF'
phosphor (#441) is clearly superior to the representative
singly coated 'RMF' phosphor (G103). The brightness
performance of the bilayer-coated singly fired zinc
5   silicate (#443), while exceeding that of the
alumina-coated 'RMF' phosphor (G103), is about 2% below
that of the rare-earth Type 2293 control, at 1000 hours of
lamp operation. However, by way of comparison a singly
fired (smaller particle) willemite phosphor with only the
10 alumina coating (i.e., without the intervening layer of
silica) is completely unsuitable for use in triblend
applications because its brightness is about 10% below
that of the corresponding alumina/silica-coated phosphor
(i.e., less than 4500 lumens initial brightness in a
15 40WT12 fluorescent lamp), as shown in Table 12.

The use of the bilayer-coated phosphor provides a
substantial cost savings over the rare-earth blends in the
examples cited above since the tri-phosphor blend
represents the major cost of the lamp and, as Table 14
20 shows, the green component comprises over 30% of the
tri-phosphor blend.

Further, the use of the singly fired bilayer-coated
phosphor provides even further cost savings, since the
large-particle 'RMF' material with narrow particle size
25 distribution requires two firings in its synthesis with
multiple decantations to remove the "fines" fraction.
This necessarily results in low yields (typically 60%).
However, the smaller particle material can be made using a
single-step firing followed by a washing which provides
30 much higher yields (typically 90%). Also, the smaller
particle material can easily be manufactured on
production-scale equipment. The much higher yields and
the efficiencies of scale all favor substantial cost
savings which far outweigh the cost of applying the
35 intermediate silica layer.

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  It is evident that fluorescent lamps will benefit
greatly from the use of the bilayer-coated and annealed
singly fired willemite phosphor by permitting a lower lamp
price that finds more acceptance in the marketplace.

5 Finally, while what has been described herein has
been fluorescent lamps employing CVD-coated phosphors in
single- and double-layered configurations, the scope of
this disclosure can include lamps which employ multiple
layers of phosphor coatings in the fabrication of the

10 lamp, multiple components of the blend in addition to, or
otherwise different from, the tri-phosphor blend
formulation described herein so long as they contain the
bilayer-coated willemite as one of the components, and the
use of non-CVD-coated alumina/silica-coated and annealed

15 willemite phosphor.

  While there has been shown and described what are at
present considered to be the preferred embodiments of the
invention, it will be obvious to those skilled in the art
that various changes and modifications can be made without

20 departing from the scope of the invention as defined by
the appended claims.

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CLAIMS

    1. A method for forming a continuous coating on phosphor particles in a fine phosphor powder comprising:

5   a) vaporizing a silicon containing precursor material into an inert carrier gas to form a carrier gas containing vaporized silicon precursor;

    b) passing said carrier gas containing silicon precursor through a mixture of phosphor powder and up to 1

10 percent fluidizing aid to form a fluidized bed in which the particles are suspended in the carrier gas and to envelop the fluidized particles with vapor of the silicon precursor said fluidized bed being maintained at a nearly isothermal condition;

15   c) agitating particles with agitating means in the fluidized bed while said particles are suspended in the fluidized bed and the carrier gas; and

    d) passing oxidizing gas into said fluidized bed separately from said carrier gas containing vaporized

20 silicon precursor and reacting said oxidizing gas with the vaporized silicon precursor on the particles of the phosphor powder to form a continuous coating of silica of predetermined thickness on the phosphor particles.

25   2. The method according to claim 1 wherein the silicon containing precursor material is tetramethyloxysilane.

    3. The method according to claim 1 wherein the

30 silicon containing precursor material is tetraethoxyorthosilicate.

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4.   The method according to claim 1 further
comprising:
     e) annealing the particles of phosphor obtained from
step (d).

5

5.   The method according to claim 4 further
comprising:
     f)   coating the particles of phosphor obtained from
step (e) with a continuous coating of alumina.

10

6.   The method according to claim 5 further
comprising:
     g) annealing the particles of phosphor obtained from
step (f).

15

7.   The method according to claim 1 wherein the
phosphor particles comprise a manganese activated zinc
silicate phosphor.

20   8.   The method according to claim 1 wherein the
phosphor particles comprise a calcium halophosphate
phosphor.

9.   A method for forming a continuous bi-layer
25 coating in phosphor particles in a phosphor powder
comprising:
     a) vaporizing a silicon-containing precursor
material into an inert carrier gas to form a carrier gas
containing vaporized silicon-containing precursor;
30   b) passing said carrier gas containing
silicon-containing precursor through a mixture of phosphor
powder and up to 1 percent fluidizing aid to form a
fluidized bed in which the particles are suspended in the
carrier gas and to envelop the fluidized particles with
35 vapor of silicon-containing precursor material, said
fluidized bed being maintained at a nearly isothermal

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condition and a temperature above the decomposition
temperature of the silicon-containing precursor material;

c) agitating particles with agitating means in the
fluidized bed while said particles are suspended in the
5 fluidized bed and the carrier gas;

d) passing oxidizing gas into said fluidized bed
separately from said carrier gas containing vaporized
silicon- containing precursor and reacting said oxidizing
gas with the vaporized silicon-containing precursor on the
10 particles of the phosphor powder to form a continuous
coating of silica of predetermined thickness on the
phosphor particles;

e) vaporizing an aluminum-containing precursor
material into an inert carrier gas to form a carrier gas
15 containing vaporized aluminum-containing precursor
material;

f) passing said carrier gas containing vaporized
aluminum precursor material through the phosphor powder
having a continuous coating of silica as produced by step
20 (d) to form a fluidized bed in which particles are
suspended in the carrier gas containing vaporized aluminum
precursor material and to envelop the fluidized particles
with vapor of aluminum-containing precursor material; and

g) passing oxidizing gas into said fluidized bed of
25 step (f) separately from said carrier gas containing
vaporized aluminum-containing precursor material and
reacting said oxidizing gas with the vaporized
aluminum-containing precursor material on the particles of
the phosphor powder having a continuous coating of silica
30 to form a continuous coating of alumina of predetermined
thickness on the phosphor particles having a continuous
coating of silica.

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10. The method according to claim 9 further
comprising:
    h) annealing the particles of phosphor obtained from
step (g).

5

    11. The method according to claim 9 wherein the
silicon- containing precursor comprises in
tetramethyloxysilane.

10   12. The method according to claim 9 wherein the
silicon- containing precursor comprises
tetraethoxyorthosilicate.

    13. The method according to claim 9 wherein the
15 phosphor comprises a manganese-activated zinc silicate
phosphor.

    14. The method according to claim 9 wherein the
phosphor comprises a calcium halophosphate phosphor.

20

    15. The method according to claim 9 wherein the
aluminum-containing precursor comprises aluminum
isopropoxide.

25   16. A method for forming a continuous coating on
phosphor particles in a fine phosphor powder comprising:
    a) vaporizing tetramethyloxysilane into an inert
carrier gas to form a carrier gas containing vaporized
tetramethyloxysilane;
30   b) passing said carrier gas containing
tetramethyloxysilane through a mixture of phosphor powder
and up to 1 percent fluidizing aid to form a fluidized bed
in which the particles are suspended in the carrier gas
and to envelop the fluidized particles with vapor of
35 tetramethyloxysilane, said fluidized bed being maintained
at a nearly isothermal condition;

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c) agitating particles with agitating means in the fluidized bed while said particles are suspended in the fluidized bed and the carrier gas; and

d) passing oxidizing gas into said fluidized bed separately from said carrier gas containing vaporized tetramethyloxysilane and reacting said oxidizing gas with the vaporized tetramethyloxysilane on the particles of the phosphor powder to form a continuous coating of silica of predetermined thickness on the phosphor particles.

17. The method according to claim 16 further comprising:

e) annealing the particles of phosphor obtained from step (d).

18. The method according to claim 16 further comprising:

f) coating the particles of phosphor of phosphor obtained from step (e) with a continuous conformal coating of alumina.

19. The method according to claim 16 wherein the phosphor comprises a manganese activated zinc silicate phosphor.

20. The method according to claim 16 wherein the phosphor comprises a calcium halophosphate phosphor.

21. A method for forming a continuous bi-layer coating in phosphor particles in a phosphor powder comprising:

a) vaporizing tetremethyloxysilane into an inert carrier gas to form a carrier gas containing vaporized tetramethyloxysilane;

b) passing said carrier gas containing tetramethyloxysilane through a mixture of phosphor powder

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and up to 1 percent fluidizing aid to form a fluidized bed
in which the particles are suspended in the carrier gas
and to envelop the fluidized particles with vapor of
tetramethyloxysilane, said fluidized bed being maintained
5 at a nearly isothermal condition and a temperature above
approximately 400°C;

     c) agitating particles with agitating means in the
fluidized bed while said particles are suspended in the
fluidized bed and the carrier gas;

10   d) passing oxidizing gas into said fluidized bed
separately from said carrier gas containing vaporized
tetramethyloxysilane and reacting said oxidizing gas with
the vaporized tetramethyloxysilane on the particles of the
phosphor powder to form a continuous coating of silica of
15 predetermining thickness on the phosphor particles;

     e) vaporizing an aluminum containing precursor
material into an inert carrier gas to form a carrier gas
containing vaporized aluminum containing precursor
material;

20   f) passing said carrier gas containing vaporized
aluminum precursor material through the phosphor powder
having a continuous coating of silica as produced by step
(d) to form a fluidized bed in which particles are
suspended in the carrier gas containing vaporized aluminum
25 precursor material and to envelop the fluidized particles
with vapor of aluminum containing precursor material; and

     g) passing oxidizing gas into said fluidized bed of
step (f) separately from said carrier gas containing
vaporized aluminum containing precursor material and
30 reacting said oxidizing gas with the vaporized aluminum
containing precursor material on the particles of the
phosphor powder having a continuous coating of silica to
form a continuous coating of alumina of predetermined
thickness of the phosphor particles having a continuous
35 coating of silica.

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22. The method according to claim 21 further comprising:

    h) annealing the particles of phosphor obtained from step (g).

23. The method according to claim 21 wherein the phosphor comprises a manganese activated zinc silicate phosphor.

24. The method according to claim 21 wherein the phosphor comprises a calcium halophosphate phosphor.

25. A particle of a finely-divided fluorescent lamp phosphor having a coating comprising a layer of silica which surrounds the particle.

26. A particle in accordance with claim 25 wherein the phosphor is a zinc silicate phosphor.

27. A particle in accordance with claim 25 wherein the phosphor is calcium halophosphate phosphor.

28. A particle in accordance with claim 25 wherein the coating has a thickness of greater than or equal to approximated 100 Angstroms.

29. A particle of a finely-divided fluorescent lamp phosphor having a bi-layer coating comprising a coating of alumina surrounding a coating of silica which surrounds the particle.

30. A particle in accordance with claim 29 wherein the phosphor is a zinc silicate phosphor.

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31. A particle in accordance with claim 29 wherein the phosphor is a calcium halophosphate phosphor.

32. A particle in accordance with claim 29 wherein
5 the bi-layer coating has a thickness of greater than or equal to approximated 100 Angstroms.

33. Particles of a phosphor, each phosphor particle being surrounded by a nonparticulate bi-layer coating com-
10 prising a coating of alumina surrounding a coating of silica, said particles when incorporated into a fluorescent lamp having a higher brightness than a lamp incorporating alumina coated phosphor particles.

15 34. A fluorescent lamp comprising a hermetically sealed tubular glass envelop coated with a phosphor, bases at each end of said tubular glass envelope, electrodes, support electrical leads connected to said electrodes, said electrodes coated with an electron-emission promoting
20 material, and a mercury droplet within said tubular glass envelope; said phosphor having a bi-layer coating comprising a coating of alumina surrounding a coating of silica which surrounds the phosphor.

25 35. The fluorescent lamp according to claim 34 wherein said phosphor is a manganese activated zinc silicate phosphor.

36. A high color rendition fluorescent lamp
30 comprising:
        a light transmissive envelope having two ends;
        electrodes sealed into each end of the envelope;
        an arc generating and sustaining medium which includes mercury;
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        a first layer of substantially broadband emitting
phosphor coating an inner surface of the light
transmissive envelop; and

        a second layer of phosphor overlying the first layer
5 of phosphor wherein the second layer of phosphor comprises
a mixture of red, blue and green emitting phosphors, the
green emitting phosphor having a coating of alumina and a
coating of silica.

10   37. The high color rendition fluorescent lamp
according to claim 36 wherein the green emitting phosphor
is a manganese activated zinc silicate phosphor.

        38. The high color rendition fluorescent lamp
15 according to claim 36 wherein the light transmissive
envelop is approximately 96 inches long.

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AMENDED CLAIMS
[received by the International Bureau on 20 June 1991 (20.06.91);
original claims 1-38 replaced by amended claims 1-25 (9 pages)]

1. A method for forming a continuous coating on
phosphor particles in a fine phosphor powder comprising:
    a) vaporizing a silicon containing precursor material
selected from the group consisting of tetramethyloxysilane
5   and tetraethyloxysilane into an inert carrier gas to form
a carrier gas containing vaporized silicon precursor;
    b) passing said carrier gas containing silicon precur-
sor through a mixture of phosphor powder and up to 1
percent fluidizing aid to form a fluidized bed in which
10   the particles are suspended in the carrier gas and to
envelop the fluidized particles with vapor of the silicon
precursor said fluidized bed being maintained at a nearly
isothermal condition and at a temperature above the
decomposition temperature of the silicon-containing
15   precursor;
    c) passing an oxidizing gas into said fluidized bed
separately from said carrier gas containing vaporized
silicon precursor and reacting said oxidizing gas with the
vaporized silicon precursor on the particles of the
20   phosphor powder to form a continuous coating of silica of
predetermined thickness on the phosphor particles;
    d) annealing the particles of the phosphor obtained
from step (c);
    e) vaporizing an aluminum-containing precursor material
25   selected from the group consisting of aluminum isopro-
poxide and tetramethylaluminum into an inert carrier gas
to form a carrier gas containing vaporized aluminum-
containing precursor material;
    f) passing said carrier gas containing vaporized
30   aluminum precursor material through the phosphor powder
having a continuous coating of silica as produced by step
(c) to form a fluidized bed in which particles are sus-
pended in the carrier gas containing vaporized aluminum
precursor material and to envelop the fluidized particles

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with vapor of aluminum containing precursor material said
fluidized bed being maintained at a nearly isothermal
condition, and at a temperature above the decomposition
temperature of the aluminum-containing precursor;

5   g) passing an oxidizing gas into said fluidized bed of
step (f) separately from said carrier gas containing
vaporized aluminum-containing precursor material and
reacting said oxidizing gas with the vaporized aluminum-
containing precursor material on the particles of the
10   phosphor powder having a continuous coating of silica to
form a continuous coating of alumina of predetermined
thickness on the phosphor particles having a continuous
coating of silica.

15   2.   The method according to claim 1 further
comprising:
        h) annealing the particles of the phosphor obtained
from step (g).

20   3.   The method according to claim 1 wherein the phos-
phor particles comprise a manganese activated zinc sili-
cate phosphor.

         4.   The method according to claim 1 wherein the phos-
25   phor particles comprise a calcium halophosphate phosphor.

         5.   A method for forming a continuous bi-layer
coating in phosphor particles in a phosphor powder
comprising:
30   a) vaporizing a silicon-containing precursor material
selected from the group consisting of tetramethyloxysilane
and tetraethyloxysilane into an inert carrier gas to form
a carrier gas containing vaporized silicon-containing
precursor;
35   b) passing said carrier gas containing silicon-
containing precursor through a mixture of phosphor powder
and up to 1 percent fluidizing aid to form a fluidized bed
in which the particles are suspended in the carrier gas

and to envelop the fluidized particles with vapor of
silicon-containing precursor material, said fluidized bed
being maintained at a nearly isothermal condition and a
temperature above the decomposition temperature of the
5   silicon-containing precursor material;

c) passing an oxidizing gas into said fluidized bed
separately from said carrier gas containing vaporized
silicon- containing precursor and reacting said oxidizing
gas with the vaporized silicon-containing precursor on the
10 particles of the phosphor powder to form a continuous
coating of silica of predetermined thickness on the
phosphor particles;

d) vaporizing an aluminum-containing precursor material
selected from the group consisting of aluminum isopro-
15 poxide and tetramethylaluminum into an inert carrier gas
to form a carrier gas containing vaporized aluminum-
containing precursor material;

e) passing said carrier gas containing vaporized
aluminum precursor material through the phosphor powder
20 having a continuous coating of silica as produced by step
(c) to form a fluidized bed in which particles are sus-
pended in the carrier gas containing vaporized aluminum
precursor material and to envelop the fluidized particles
with vapor of aluminum-containing precursor material said
25 fluidized bed being maintained at a nearly isothermal
condition and at a temperature above the decompositon
temperature of the aluminum containing precursor; and

f) passing an oxidizing gas into said fluidized bed of
step (e) separately from said carrier gas containing
30 vaporized aluminum-containing precursor material and
reacting said oxidizing gas with the vaporized aluminum-
containing precursor material on the particles of the
phosphor powder having a continuous coating of silica to
form a continuous coating of alumina of predetermined
35 thickness on the phosphor particles having a continuous
coating of silica.

6.   The method according to claim 5 further
comprising:

    g) annealing the particles of phosphor obtained from
step (f).

5

    7.   The method according to claim 5 wherein the
phosphor comprises a manganese-activated zinc silicate
phosphor.

10   8.   The method according to claim 5 wherein the
phosphor comprises a calcium halophosphate phosphor.

    9.   A method for forming a continuous coating on phos-
phor particles in a fine phosphor powder comprising:

15   a) vaporizing a silicon containing precursor material
selected from the group consisting of tetramethyloxysilane
and tetraethyloxysilane into an inert carrier gas to form
a carrier gas containing vaporized silicon-containing
precursor material;

20   b) passing said carrier gas containing silicon-
containing precursor material through a mixture of phos-
phor powder and up to 1 percent fluidizing aid to form a
fluidized bed in which the particles are suspended in the
carrier gas and to envelop the fluidized particles with

25 vapor of silicon-containing precursor material, said
fluidized bed being maintained at a nearly isothermal
condition and at a temperature above the decomposition
temperature of the silicon-containing precursor;

    c) agitating particles with agitating means in the

30 fluidized bed while said particles are suspended in the
fluidized bed and the carrier gas; and

    d) passing an oxidizing gas into said fluidized bed
separately from said carrier gas containing vaporized
tetramethyloxysilane and reacting said oxidizing gas with

35 the vaporized tetramethyloxysilane on the particles of the
phosphor powder to form a continuous coating of silica of
predetermined thickness on the phosphor particles;

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e) annealing the particles of the phosphor obtained from step (d); and

f) vaporizing an aluminum-containing precursor material selected from the group consisting of aluminum isopropoxide and tetramethylaluminum into an inert carrier gas to form a carrier gas containing vaporized aluminum-containing precursor material;

g) passing said carrier gas containing vaporized aluminum precursor material through the phosphor powder having a continuous coating of silica as produced by step (c) to form a fluidized bed in which particles are suspended in the carrier gas containing vaporized aluminum precursor material and said fluidized bed being maintained at a nearly isothermal condition and at a temperature above the decomposition temperature of the aluminum-containing precursor; and

h) passing an oxidizing gas into said fluidized bed of step (f) separately from said carrier gas containing vaporized aluminum-containing precursor material and reacting said oxidizing gas with the vaporized aluminum-containing precursor material on the particles of the phosphor powder having a continuous coating of silica to form a continuous coating of alumina of predetermined thickness on the phosphor particles having a continuous coating of silica.

10. The method according to claim 9 wherein the phosphor comprises a manganese activated zinc silicate phosphor.

11. The method according to claim 9 wherein the phosphor comprises a calcium halophosphate phosphor.

12.   A method for forming a continuous bi-layer
coating in phosphor particles in a phosphor powder
comprising:

   a) vaporizing a silicon containing precursor material
5 selected from the group consisting of tetramethyloxysilane
and tetraethyloxysilane into an inert carrier gas to form
a carrier gas containing vaporized silicon-containing
precursor material;

   b) passing said carrier gas containing silicon-
10 containing precursor material through a mixture of phos-
phor powder and up to 1 percent fluidizing aid to form a
fluidized bed in which the particles are suspended in the
carrier gas and to envelop the fluidized particles with
vapor of silicon-containing precursor material, said
15 fluidized bed being maintained at a nearly isothermal
condition and at a temperature above the decomposition
temperature of the silicon-containing precursor;

   c) agitating particles with agitating means in the
fluidized bed while said particles are suspended in the
20 fluidized bed and the carrier gas;

   d) passing an oxidizing gas into said fluidized bed
separately from said carrier gas containing vaporized
silicon-containing precursor material and reacting said
oxidizing gas with the vaporized silicon-containing
25 precursor material on the particles of the phosphor powder
to form a continuous coating of silica of predetermining
thickness on the phosphor particles;

   e) vaporizing an aluminum containing precursor material
selected from the group consisting of aluminum isopro-
30 poxide and trimethylaluminum into an inert carrier gas to
form a carrier gas containing vaporized aluminum contain-
ing precursor material;

   f) passing said carrier gas containing vaporized alumi-
num precursor material through the phosphor powder having
35 a continuous coating of silica as produced by step (d) to
form a fluidized bed in which particles are suspended in
the carrier gas containing vaporized aluminum precursor

material and to envelop the fluidized particles with vapor
of aluminum containing precursor material said fluidized
bed being maintained at a nearly isothermal condition and
at a temperature above the decomposition temperature of
the aluminum-containing precursor; and

    g) passing an oxidizing gas into said fluidized bed of
step (f) separately from said carrier gas containing
vaporized aluminum containing precursor material and
reacting said oxidizing gas with the vaporized aluminum
containing precursor material on the particles of the
phosphor powder having a continuous coating of silica to
form a continuous coating of alumina of predetermined
thickness of the phosphor particles having a continuous
coating of silica.

    13. The method according to claim 12 further
comprising:
    h) annealing the particles of phosphor obtained from
step (g).

    14. The method according to claim 12 wherein the
phosphor comprises a manganese activated zinc silicate
phosphor.

    15. The method according to claim 12 wherein the
phosphor comprises a calcium halophosphate phosphor.

    16. A particle of a finely-divided fluorescent lamp
phosphor having a bi-layer coating comprising a coating of
alumina surrounding a coating of silica which surrounds
the particle.

    17. A particle in accordance with claim 16 wherein
the phosphor is a zinc silicate phosphor.

-55-

18.   A particle in accordance with claim 16 wherein the phosphor is a calcium halophosphate phosphor.

19.   A particle in accordance with claim 16 wherein the bi-layer coating has a thickness of greater than or equal to approximated 100 Angstroms.

20.   Particles of a phosphor, each phosphor particle being surrounded by a nonparticulate bi-layer coating comprising a coating of alumina surrounding a coating of silica, said particles when incorporated into a fluorescent lamp having a higher brightness than a lamp incorporating alumina coated phosphor particles.

21.   A fluorescent lamp comprising a hermetically sealed tubular glass envelop coated with a phosphor, bases at each end of said tubular glass envelope, electrodes, support electrical leads connected to said electrodes, said electrodes coated with an electron-emission promoting material, and a mercury droplet within said tubular glass envelope; said phosphor having a bi-layer coating comprising a coating of alumina surrounding a coating of silica which surrounds the phosphor.

22.   The fluorescent lamp according to claim 21 wherein said phosphor is a manganese activated zinc silicate phosphor.

23.   A high color rendition fluorescent lamp comprising:
     a light transmissive envelope having two ends;
     electrodes sealed into each end of the envelope;
     an arc generating and sustaining medium which includes mercury;

a first layer of substantially broadband emitting
phosphor coating an inner surface of the light transmis-
sive envelop; and

a second layer of phosphor overlying the first layer of
5   phosphor wherein the second layer of phosphor comprises a
mixture of red, blue and green emitting phosphors, the
green emitting phosphor having a coating of alumina and a
coating of silica.

10   24.   The high color rendition fluorescent lamp accord-
ing to claim 23 wherein the green emitting phosphor is a
manganese activated zinc silicate phosphor.

          25.   The high color rendition fluorescent lamp accord-
15   ing to claim 23 wherein the light transmissive envelop is
approximately 96 inches long.
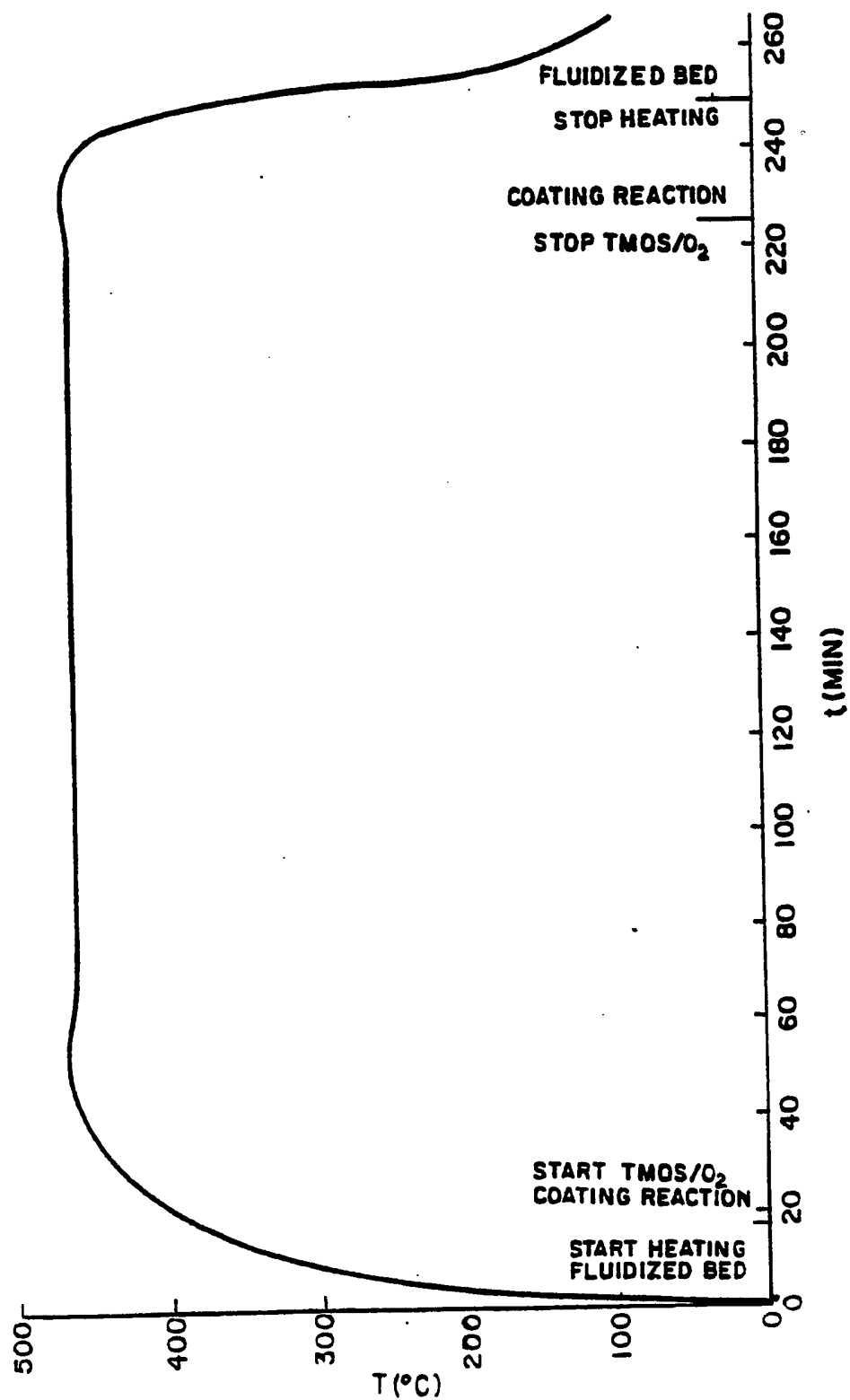
20

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30

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FIG. 1

FIG. 2

FIG. 3

FIG. 4

PHOSPHOR
GRAIN

ALUMINA
LAYER

SILICA
LAYER

FIG. 5

38 40   12   10

26   18   14   22   32

34   16   36

30   20   24   28   32

FIG.6

12   10

40   38

FIG.7
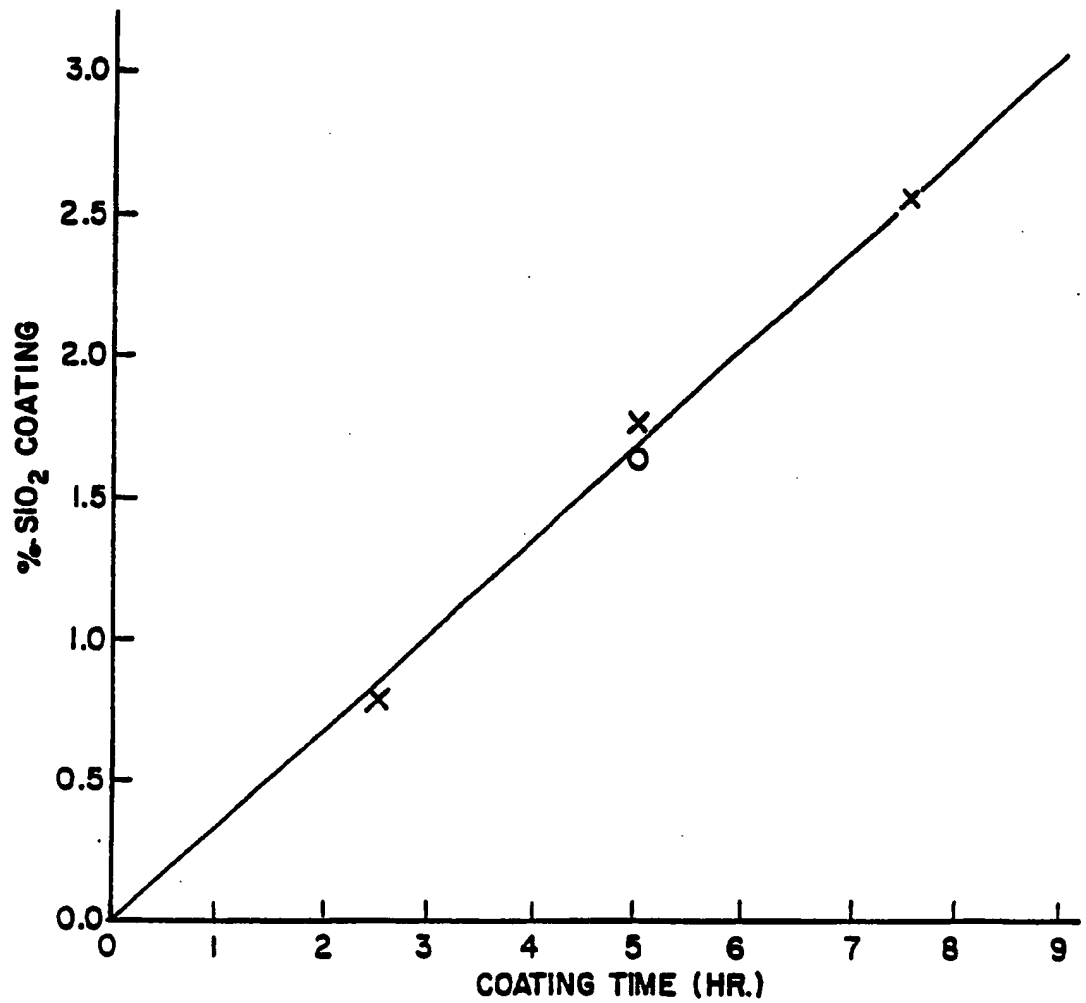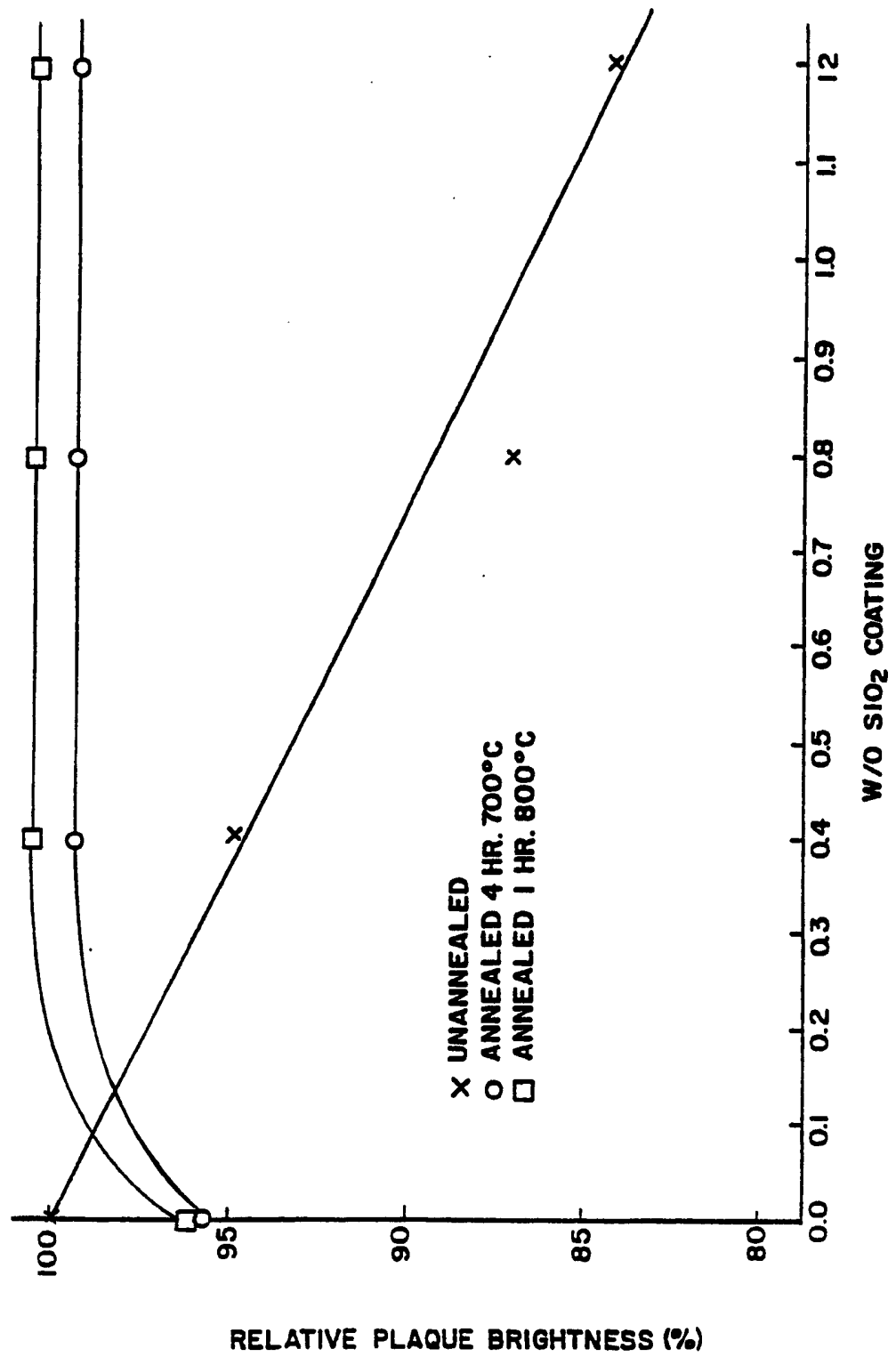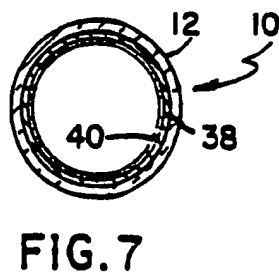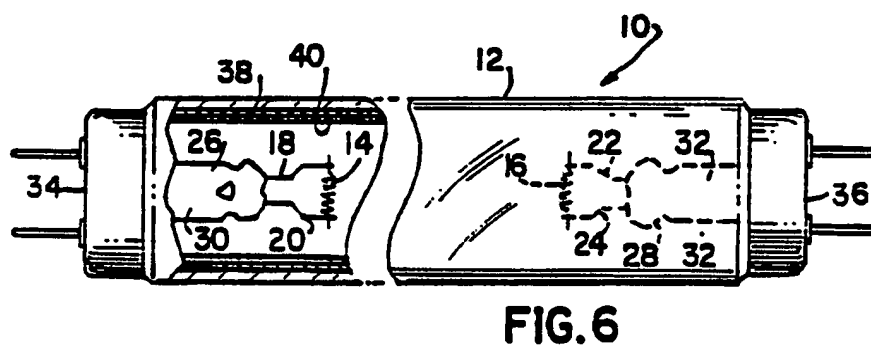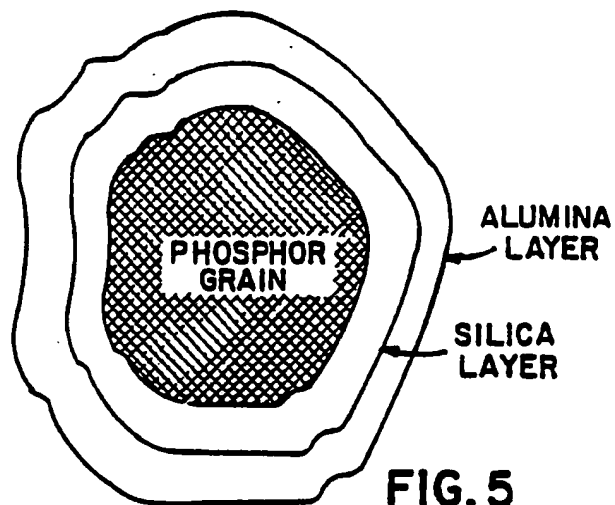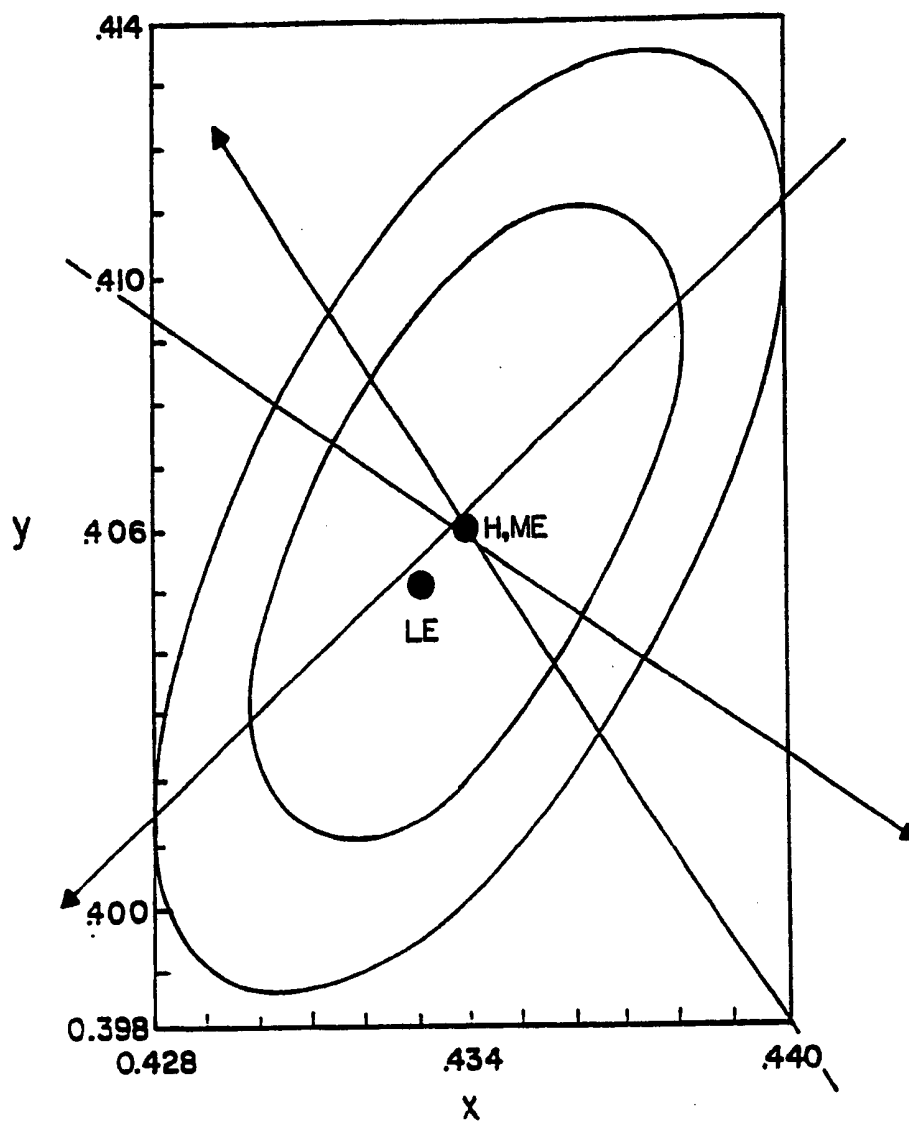
FIG. 8
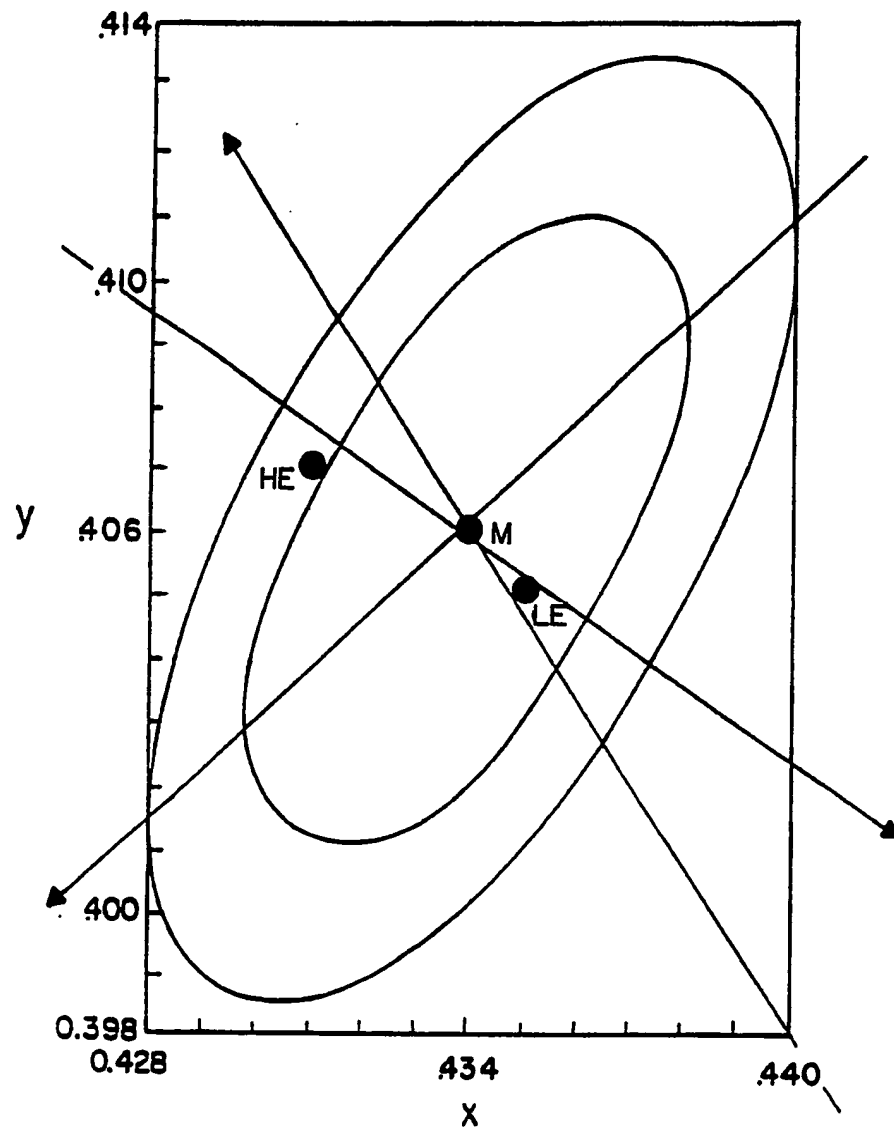
FIG.9
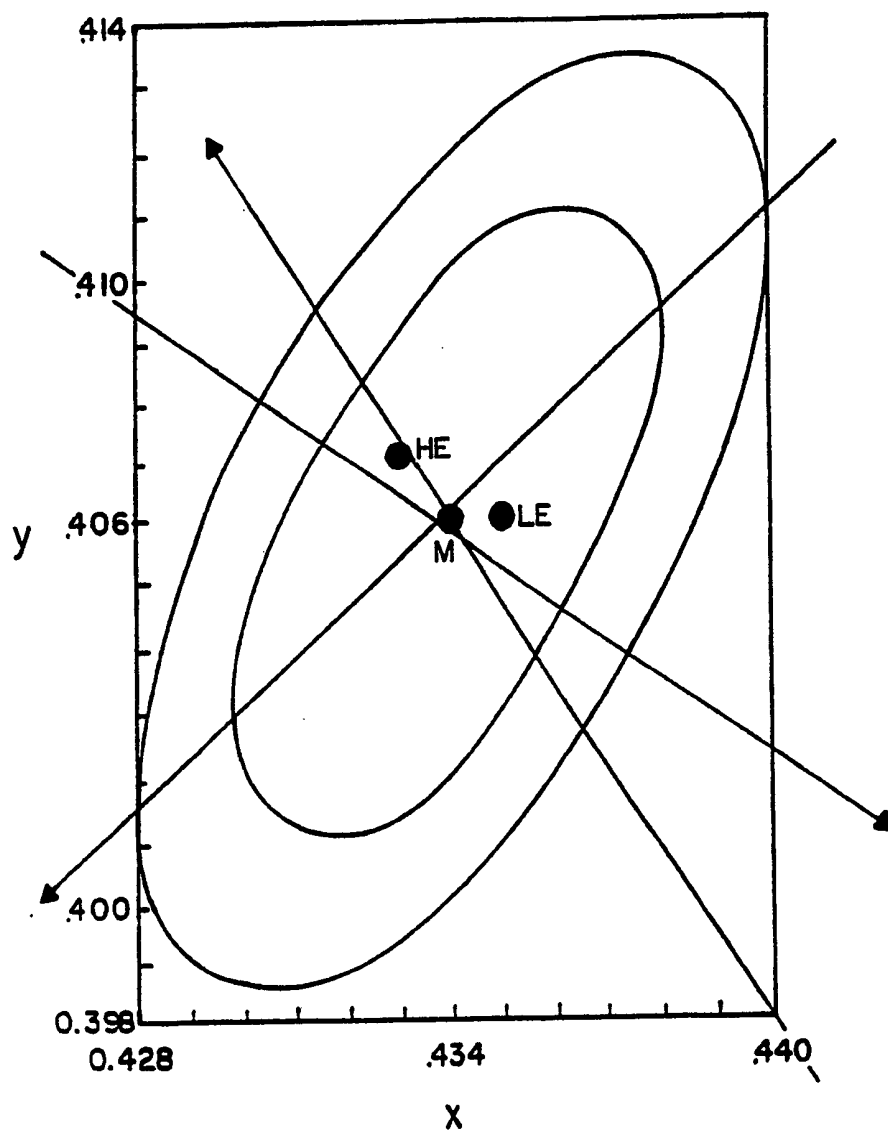
FIG. 10

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]
According to International Patent Classification (IPC) or to both National Classification and IPC
IPC5: C 09 K 11/02, H 01 J 61/44

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 09 K; F 21 V; H 01 J

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category*	Citation of Document,[11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	EP, A2, 0318272 (LUMEL, INC) 31 May 1989, see page 3, line 45 - line 48	25
Y		1
	--	
X	US, A, 3408223 (S.R. SHORTES) 29 October 1968, see column 3, line 58 - line 59; abstract	25,26
	--	
X	DE, B, 1028262 (AUERGESELLSCHAFT AKTIENGESELLSCHAFT) 17 April 1958, see column 3, line 5 - line 9	25,27
	--	

* Special categories of cited documents:[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
5th April 1991	1 7. 05. 91
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	F.W. HECK

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
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